



**AFRL-RX-WP-TP-2009-4084**

**THERMAL ANALYSIS OF THE EFFECT OF OXYGEN  
CONTAMINATION ON UNDERCOOLING OF  
Zr-Al-Ni-Cu, Cu-Zr-Ti, and Cu-Ni-Zr-Ti METALLIC  
GLASSES (PREPRINT)**

**W.S. Sanders, D.B. Miracle, and S.A. Firdosy**

**Metals Branch**

**Metals, Ceramics and NDE Division**

**APRIL 2009**

**Approved for public release; distribution unlimited.**

*See additional restrictions described on inside pages*

**STINFO COPY**

**AIR FORCE RESEARCH LABORATORY  
MATERIALS AND MANUFACTURING DIRECTORATE  
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750  
AIR FORCE MATERIEL COMMAND  
UNITED STATES AIR FORCE**

<b>REPORT DOCUMENTATION PAGE</b>				<i>Form Approved</i> OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b>					
<b>1. REPORT DATE (DD-MM-YY)</b> April 2009		<b>2. REPORT TYPE</b> Journal Article Preprint		<b>3. DATES COVERED (From - To)</b> 01 April 2009- 01 April 2009	
<b>4. TITLE AND SUBTITLE</b> THERMAL ANALYSIS OF THE EFFECT OF OXYGEN CONTAMINATION ON UNDERCOOLING OF Zr-Al-Ni-Cu, Cu-Zr-Ti, and Cu-Ni-Zr-Ti METALLIC GLASSES (PREPRINT)				<b>5a. CONTRACT NUMBER</b> In-house	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b> 62102F	
<b>6. AUTHOR(S)</b> W.S. Sanders and D.B. Miracle (AFRL/RXLMD) S.A. Firdosy (California State Polytechnic University)				<b>5d. PROJECT NUMBER</b> 4347	
				<b>5e. TASK NUMBER</b> RG	
				<b>5f. WORK UNIT NUMBER</b> M02R4000	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;">           Metals Branch (RXLMD)            Metals, Ceramics and NDE Division            Materials and Manufacturing Directorate            Wright-Patterson Air Force Base, OH 45433-7750            Air Force Materiel Command, United States Air Force         </div> <div style="width: 45%;">           Department of Chemical and Materials Engineering            California State Polytechnic University            Pomona, CA 91768         </div> </div>				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  AFRL-RX-WP-TP-2009-4084	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force				<b>10. SPONSORING/MONITORING AGENCY ACRONYM(S)</b> AFRL/RXLMD	
<b>11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)</b> AFRL-RX-WP-TP-2009-4084					
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b> To be submitted to Intermetallics PAO Case Number and clearance date: 88ABW-2009-1040, 17 March 2009. The U.S. Government is joint author on this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.					
<b>14. ABSTRACT</b> Oxygen impurity levels have been varied in Zr65Al17.5(Cu17.5Ni10), Cu60Zr30Ti10, and (Cu47Ni8)Zr11Ti34 glass forming alloys, and their effect has been characterized by differential scanning calorimetry and x-ray diffraction. Results indicate that these alloys exhibit varying amounts of sensitivity to oxygen. In Zr65Al17.5(Cu17.5Ni10), ΔTx decreases dramatically from over 100K to 55K when 1.0 a% oxygen is added; in (Cu47Ni8)Zr11Ti34, ΔTx remains relatively constant at 45K up to 1.2 at% oxygen; in Cu60Zr30Ti10, ΔTx first increases from 31K to 38K as oxygen concentration increases for 0.32 to 0.80 at%, and then ΔTx decreases again at higher oxygen levels. These results indicate that oxygen addition to some amorphous metal compositions could be regarded as a beneficial alloying element to improve thermal stability.					
<b>15. SUBJECT TERMS</b> B glasses, metallic; B thermal stability					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT:</b> SAR	<b>18. NUMBER OF PAGES</b> 26	<b>19a. NAME OF RESPONSIBLE PERSON (Monitor)</b> Jonathan Spowart <b>19b. TELEPHONE NUMBER (Include Area Code)</b> N/A
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			

# **Thermal analysis of the effect of oxygen contamination on undercooling of Zr-Al-Ni-Cu, Cu-Zr-Ti, and Cu-Ni-Zr-Ti metallic glasses**

W.S. Sanders <sup>a,\*</sup>, D.B. Miracle <sup>a</sup>, S.A. Firdosy <sup>b</sup>

<sup>a</sup> Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA

<sup>b</sup> Department of Chemical and Materials Engineering, California State Polytechnic University, 3801 W. Temple Avenue, Pomona, CA 91768

**Corresponding Author:** Daniel Miracle

2230 Tenth Street, Wright-Patterson AFB, OH USA 45433

[Daniel.miracle@wpafb.af.mil](mailto:Daniel.miracle@wpafb.af.mil)

+937.255.9833

## **Abstract**

Oxygen impurity levels have been varied in  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  glass forming alloys, and their effect has been characterized by differential scanning calorimetry and x-ray diffraction. Results indicate that these alloys exhibit varying amounts of sensitivity to oxygen. In  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\Delta T_x$  decreases dramatically from over 100K to 55K when 1.0 at% oxygen is added; in  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$ ,  $\Delta T_x$  remains relatively constant at 45K up to 1.2 at% oxygen; in  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ ,  $\Delta T_x$  first increases from 31K to 38K as oxygen concentration increases from 0.32 to 0.80 at%, and then  $\Delta T_x$  decreases again at higher oxygen levels. These results indicate that oxygen addition to some amorphous metal compositions could be regarded as a beneficial alloying element to improve thermal stability.

## **Keywords:**

B glasses, metallic; B thermal stability

## 1. Introduction

Extensive development has been conducted to optimize the glass-forming ability of numerous metallic glass systems, and a wide body of literature exists for these systems [1]. The glass-forming ability of metallic glasses has been shown to be highly dependent on the levels of oxygen contamination in the system; impurity levels of only a fraction of an atomic percent can dramatically reduce the supercooled liquid range  $\Delta T_x$  and change the crystallization process [2 - 4]. During processing, the cleanliness of the molten alloy is important; impurities can induce nucleation of crystalline phases during cooling, which also increases the critical cooling rate for glass formation [2, 3].

Many authors have reported the effect of oxygen on crystal nucleation in undercooled melts of Zr-based alloys.  $\text{Zr}_{65}\text{Al}_{17.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ —compositions throughout the manuscript are given in atomic percent and follow the convention described in [5]—exhibits one of the highest  $\Delta T_x$  value reported [6] and has been shown to exhibit a very sensitive reaction to oxygen impurities in the melt. Oxygen affects the critical cooling rate for glass formation [2] and it has been shown to influence the crystallization behavior of Zr-based metallic glasses. Oxygen induces the formation of metastable phases, which reduces the thermal stability of the glass. Further studies have shown that oxygen enhances the crystallization reaction [7] and the phases formed during crystallization of Zr alloys are highly dependent on the oxygen content [8]. Oxygen causes a dramatic reduction in the supercooled liquid region that is accompanied by a change in the crystallization sequence, leading to reduced stability of the supercooled liquid [9, 10]. The  $\Delta T_x$  dropped from 120 K at 0.28 at% oxygen to 70 K at 0.58 at% oxygen. The oxygen-triggered nucleation of a nanocrystalline metastable f.c.c.  $\text{NiZr}_2$ -type phase was found to be the initial step of crystallization from the undercooled liquid. These nanocrystals then act as heterogeneous nucleation sites for crystallization of other stable intermetallic phases [10].

Little work has been done on systems other than  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ .  $\text{Zr}_{55}\text{Al}_{10}(\text{Cu}_{30}\text{Ni}_5)$  was found to be less sensitive to oxygen content than  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ —the  $\Delta T_x$  decreased by only 25 K with the addition of approximately 0.5 at% oxygen [10]. Zr-Cu based systems were studied, and [7] reported a similar trend in  $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{27.5}$  where oxygen decreases the undercooled region. However, Murty et al. [7] reported that in the binary alloy  $\text{Zr}_{66.7}\text{Cu}_{33.3}$ , the addition of oxygen actually increases the undercooled liquid region and reported a more stable amorphous alloy with increased oxygen content. In a study of gas atomized  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{33}\text{Si}_1$  powders [11], the fraction of amorphous phase decreased from 99% to 52% and the crystallization temperature decreased as the oxygen content was increased from 0.5 at% to 2.7 at%. In  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ , the crystallization temperature decreased from 277 °C to 263 °C with the addition of 0.5 at% oxygen [12].

Additional literature exists regarding ways to mitigate or undo the effect of oxygen contamination. Fluxing with  $\text{B}_2\text{O}_3$  is utilized quite successfully on Pd- and Fe-based systems. The critical cooling rate is reduced an order of magnitude in Pd-Cu-Ni-P [1, 13]. The glass-forming alloy  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  (tradename Metglas2826) has been extensively studied in the literature [14]. Using  $\text{B}_2\text{O}_3$  as a flux, the  $T_g$  was reduced an average of 19°C and the  $T_x$  increased an average of 17°C compared to the values previously reported. Thus, removal of heteronucleants from the melt, mainly in the form of oxide inclusions, increased  $\Delta T_x$  an average of 36°C and the critical cooling rate was reduced three orders of magnitude. Other studies have sought to remove oxygen from the material by direct electrochemical reduction in a molten salt bath. In  $\text{Zr}_{55}\text{Al}_{10}(\text{Cu}_{30}\text{Ni}_5)$ , electrochemical processing removed a small amount of oxygen impurities, with a resulting small increase in glass-forming ability [15]. In other schemes, additional elements are added to mitigate the effects of oxygen impurities. A small amount of Y (2-4 at%) has been shown to improve the glass-forming ability of  $\text{Zr}_{55}\text{Al}_{15}(\text{Cu}_{20}\text{Ni}_{10})$  when low purity materials are used [16]. The addition of 0.5 or 1.0% Ti in  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  [12] is shown to prevent the reduction in crystallization temperature when contaminated with up to 1% oxygen;

however, it should be noted that the author argues that the Ti microadditions may not act as oxygen scavengers as suggested by [16-19]. It was shown that adding 0.1% B + 0.2% Si + 0.1% Sn improved the glass formability the  $\text{Zr}_{52.5}(\text{Al}_{10}\text{Ti}_5)(\text{Cu}_{17.9}\text{Ni}_{14.6})$  and provided maximum fracture strength [19]. The addition of 1% Si in  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{33}\text{Si}_1$  was shown to improve the alloy's glass-forming ability in the presence of contaminants such as O and C [11, 17].

Extensive work has shown that oxygen contamination dramatically reduces the glass forming ability of Zr-based alloys (there is one exception in the literature where oxygen improves glass forming ability in the binary Zr-Cu glass forming system [7]). Other scattered studies have shown that oxygen is detrimental in additional systems as well. Some data also exists on ways to mitigate the detrimental effects of oxygen by microalloying additional elements. However, a detailed study to quantify the effect of oxygen contamination across a broad range of bulk metallic glass forming systems has not been conducted. This work aims to begin addressing this need by determining the relative magnitude of the detriment (or benefit) of oxygen levels on glass forming ability of various glass-forming systems.  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  have reported critical thickness values of 9 mm, 4.5 mm, and 4 mm, respectively [3, 20]. These three alloys have  $T_g$  and  $T_x$  values below 873 K. The study of these systems allows the quantification of  $\Delta T_x$  versus oxygen concentration on two new Cu-based systems and a comparison to a well-studied Zr-based alloy. From a practically oriented perspective,  $\Delta T_x$  is a useful metric because a larger supercooled liquid regime provides greater processing flexibility during manufacturing. Since the effect of oxygen contamination in  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  has been studied previously [10], it was included in this work to provide a baseline for the observations.

## 2. Experimental

Three sets of alloys were prepared to the nominal compositions of  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  by arc-melting each of the pure elements under a titanium-gettered atmosphere. Starting materials used were: Al pellets, 99.999%; Cu shot, 99.999%; Ni pellets, 99.995%; Ti pellets, 99.995%; and Zr sponge, 99.8%. A modified MAM-1 Mini-Arc Melter (Johannas Otto, Germany) was used to produce 2-6 g alloyed ingots of each composition. Each ingot was flipped typically 4-5 times in a titanium-gettered, high-purity argon atmosphere (after three cycles of a vacuum pumpdown to 30 millitorr). Each ingot was then individually contaminated with oxygen to varying levels by remelting in a less-than-pure atmosphere containing oxygen. The oxygen-containing atmosphere was achieved by establishing a vacuum of 1000 millitorr and backfilling with argon (in this case a Ti getter was not used). A desired amount of oxygen was added by monitoring of the ingot mass after each melt (in a 2 g ingot, 0.1 at% oxygen corresponded to approximately 1.0 mg increase in mass). The ingot was remelted until the increased mass (due to oxygen) indicated the desired oxygen level was reached. Each alloyed ingot was cast into a 0.5 mm X 5 mm X 30 mm strip using a water-cooled copper mold in the MAM-1. Several of the  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  ingots with an oxygen content of 1.5 at% were cast into a strip 0.25 mm thick. To determine glass transition temperature and crystallization temperature, several samples from each cast sheet were analyzed using a Q-1000 Differential Scanning Calorimeter (TA Instruments, New Castle, DE) at a heating rate of  $20 \text{ K min}^{-1}$  from room temperature to 873K. The activation energy for crystallization was calculated for a few compositions by running additional samples at heating rates of 5, 10, 20, and  $50 \text{ K min}^{-1}$  and applying a Kissinger analysis to the measured shift in crystallization temperature. Oxygen content was determined for each alloy ingot using a LECO TC600 (Leco Corporation, St. Joseph, MI). Roughly 7 different levels of oxygen were studied in each of the three alloy systems.

### 3. Results

The DSC traces for selected alloys from  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  are shown in Figures 1-3. In all curves, exothermic reactions are indicated by positive heat flows. The values for glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_x$ ) were determined using the TA Instruments software.  $T_g$  is measured at the onset point of the glass transition region and  $T_x$  is measured as the onset temperature of the crystallization reaction. Typically, the  $T_g$  of a given DSC curve can vary up to  $\pm 2^\circ\text{C}$  depending on the tangent construction, but the measurement of  $T_x$  in an alloy has an error less than  $0.5^\circ\text{C}$ . In Figure 1, the  $T_g$  of  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  gradually increases with oxygen content, while the  $T_x$  dramatically decreases. The main exothermic peaks for 0.35, 0.40, and 0.44 at% oxygen exhibit small shoulders just after the peak temperature is reached, indicating the close superposition of two peaks. The scan of the 0.32 % oxygen sample shows a single peak, but at higher oxygen contents a small, secondary crystallization peak develops. In Figure 2, only three oxygen content levels are shown for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ . Ingots with additional oxygen levels were produced, but could not be cast properly for reasons that will be discussed in a following section. From 0.32 to 0.80% oxygen the  $T_g$  gradually increases and the  $T_x$  exhibits a more dramatic increase. At 1.26% oxygen, both  $T_g$  and  $T_x$  decrease. For  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  in Figure 3, the glass transition and first crystallization peak increase in temperature up to 0.68% oxygen and then remain constant. The temperature of the second crystallization peak increases up to 0.42% oxygen, then decreases. The temperature of the third crystallization peak remains constant up to 0.42% oxygen and then decreases to a constant level above 0.68% oxygen.

Figure 4 shows plots of  $T_g$ ,  $T_x$ , and  $\Delta T_x$ ,  $\Delta H_{\text{first}}$  (heat of crystallization of first peak) and  $\Delta H_{\text{all}}$  (heat of crystallization of all peaks) for the three alloy systems. In this figure, the trends of each of the parameters can be more easily observed and compared. In  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $T_g$  gradually increases with oxygen content and both  $T_x$  and  $\Delta T_x$  decrease with increasing oxygen.

As the oxygen level is increased, the heat of crystallization of the first peak decreases. However, the total heat of crystallization remains relatively constant since the energy of crystallization of the second peak increases. In  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ ,  $T_g$  and  $T_x$  exhibit a slight increase from 0.32 to 0.80 at% oxygen and then remain relatively constant. A split in  $T_x$  occurs above 1% oxygen; multiple DSC scans of material from the same cast strip exhibited this shift. This is explained further in the Discussion. This splitting is also observed in the  $\Delta T_x$  values. The heat of crystallization remains relatively constant, with a decrease only at 1.26% oxygen. In  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$ , the  $T_g$  and  $T_x$  gradually increase, while the  $\Delta T_x$  remains relatively constant up 1.2% oxygen. The total heat of crystallization reaches a maximum at 0.4% oxygen while the heat of crystallization of the first peak is constant up to 0.4% oxygen.

The activation energy for crystallization was calculated using a Kissinger analysis of the first crystallization peak and is shown in Figure 5 for selected compositions in each alloy system. The activation energy remains relatively constant for  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  and increases slightly with increasing oxygen for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ . An interesting behavior is shown for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  where the activation energy increases from 226 to nearly 331 KJ/mol at 0.4% oxygen and then decreases with higher amounts of oxygen.

#### 4. Discussion

The thermal behavior of  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  measured here agrees with previously reported results [10]. The decrease in crystallization temperature is shown to occur due to oxygen-triggered formation of metastable quasicrystalline and fcc  $\text{NiZr}_2$ -type phases, deteriorating the thermal stability of the alloy [21]. These metastable phases then act as heterogeneous nuclei for other crystalline phases, indicated by the second DSC peak in Figure 1 that develops at oxygen contents above 0.4%. Quasicrystal formation was found to occur in the first step, regardless of oxygen content level. The splitting of the crystallization events in Figure 1 indicates that at

oxygen contents above 0.4%, the mode of crystallization changes from simultaneous precipitation of several phases to a successive stepwise transformation into the equilibrium phases [21]. Eckert was able to unambiguously index X-ray patterns to find that, below 0.4% oxygen, the first crystallization products are  $\text{Zr}_6\text{NiAl}_2 + \text{CuZr}_2 + \text{quasicrystal}$ . However, at 0.4% oxygen and above, the first crystallization products are  $\text{CuZr}_2 + \text{quasicrystal} + \text{fcc NiZr}_2\text{-type}$ ; the  $\text{Zr}_6\text{NiAl}_2$  phase does not crystallize until a higher temperature, thus explaining the second crystallization peak. Regardless of oxygen level, the final crystallization products were found to be the same in all cases. Further, the amount of quasicrystalline phase first nucleated is found to increase as the oxygen content is increased. The heat of crystallization of the first peak drops uniformly with oxygen content, but the heat of crystallization of the second peak increases to a constant level above 0.4% oxygen. Based on this data, the slope of  $T_x$  vs. oxygen content (Figure 4) changes at an oxygen level above 0.4%. Thus, increasing oxygen promotes formation of the quasicrystalline phase, which inhibits formation of  $\text{Zr}_6\text{NiAl}_2$  above 0.4% oxygen, acting to stabilize the undercooled liquid. Although Gebert argues [10] that the oxygen causes a change of the crystallization sequence which points to a reduced stability of the liquid, it could instead be argued that oxygen promotes the formation of quasicrystalline phases, stabilizing the supercooled liquid against the formation of  $\text{Zr}_6\text{NiAl}_2$  and stabilizing the decrease in crystallization temperature. Also noteworthy is the activation energy as a function of oxygen content, which increases from 226 to 331 KJ/mol at 0.44% oxygen and then plateaus and decreases at higher oxygen levels. This could provide further evidence that the  $\text{Zr}_6\text{NiAl}_2$  phase becomes increasingly difficult to nucleate, while the activation energy for quasicrystalline and  $\text{CuZr}_2$  phases decreases with oxygen content.

As seen in Figure 4 for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ , the glass transition temperature increases with increasing oxygen content. Since oxygen has a smaller atomic radius than the other elements in the alloy, it increases the packing density of the amorphous phase [7, 21]. Further analysis shows that oxygen can form densely-packed octahedral Zr-O clusters. First proposed by

Altounian [22], a cluster of six Zr atoms surrounding one oxygen atom is very efficiently packed according to the model published in [23], thus increasing local packing density. It is interesting to note that the  $T_g$  seems to remain relatively constant (within measurement error) up to 0.4% oxygen. Overall, the increase in  $T_g$  and the decrease in  $T_x$  decrease the stability of the undercooled liquid (as measured by  $\Delta T_x$ ) with increasing levels of oxygen.

In the crystallization sequence for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  as reported by [24], the first peak corresponds to crystallization of a nanometer-sized bcc CuZr phase. The second peak indicates crystallization of a large cubic phase resembling the main equilibrium phase  $\text{Cu}_{10}\text{Zr}_7$ . During the third and final crystallization step, which occurs at a temperature above 750°C (above the maximum operating temperature of the DSC unit used in the present study), the metastable large cubic phase is transformed into the equilibrium phases  $\text{Cu}_{10}\text{Zr}_7 + \text{Cu}_8\text{Zr}_3 + \text{Cu}_3\text{Ti}_2$ . Unlike  $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{17.5}\text{Ni}_{10}$ , the activation energy for the first crystallization peak (Figure 5) increases only slightly with oxygen content, indicating that the crystallization reactions may not change with oxygen content.

As seen in Figure 4, the  $T_g$  of  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  remains relatively constant. Although there appears to be a slight increase from 0.32 to 0.8% oxygen, the difference is within the  $T_g$  measurement error. The crystallization temperature increases by approximately 13°C as the oxygen content increases from 0.32 to 0.8%, and then splits into two crystallization temperatures. A shift in crystallization temperature occurred in different samples taken from the same cast strip at high oxygen concentrations (above 1 at%). As seen in Figure 6, material analyzed from different locations on the strip with an oxygen content of 1.26 at% exhibit different behavior. In the top curve, the crystallization temperature is approximately 480°C,  $T_x$  for the bottom curve is approximately 470°C, and two initial crystallization reactions can be seen in the center curve at both 470 and 480°C. This split (or shift) in the crystallization temperatures was persistent across all samples above 1.0% oxygen. Further, the  $T_g$  was difficult to measure and there appeared to be two glass transition temperatures, one at 433°C and one at 440°C. This indicates that the sample may not

have been homogeneously cast, possibly exhibiting two different amorphous phases. It was difficult to uniformly heat the ingot on the water-cooled copper hearth because Cu-Ti-Zr has a high thermal conductivity due to its high copper content. During heating with the arc a temperature gradient could be observed—the top of the ingot had a bright glow and the bottom was much darker, even when the arc current was increased to the maximum setting. Additional ingots (and additional oxygen content levels) could not be cast because the mold started to loosen, detrimentally affecting casting quality.  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  was the last alloy composition examined, so this problem did not affect the other compositions.

The samples of  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  with 1.5 at% oxygen were cast in a mold 250  $\mu\text{m}$  thick. The data from these samples is also shown in Figure 4. The only observable difference between 250  $\mu\text{m}$  thick and 500  $\mu\text{m}$  thick cast samples is in the heat of crystallization. The 1.5% oxygen sample was 250  $\mu\text{m}$  thick and, compared to the 1.26% sample (500  $\mu\text{m}$  thick), had a higher cooling rate, causing a higher volume fraction of amorphous phase.

The results in Figure 4 for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  show an increase in  $T_x$  from 471°C to 484°C as the oxygen increases from 0.32% to 0.80%. This, in combination with the relatively constant  $T_g$ , leads to a  $\Delta T_x$  increase of 9 K from 0.32% to 0.80% oxygen indicating slightly improved stability of the metallic glass system. This is the first ternary metallic glass that shows an increase in  $\Delta T_x$  with increasing oxygen content. [7] showed that increasing oxygen from 0.14% to 0.82% in  $\text{Zr}_{66.7}\text{Cu}_{33.3}$  increases  $\Delta T_x$  by 12 K.

For  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  in Figure 4, both  $T_g$  and  $T_x$  increase about 10 K as oxygen is increased from 0.20% to 0.60%. The marginal increase in  $T_g$  could indicate an interaction between oxygen and zirconium or titanium to increase local packing density as was seen with  $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{17.5}\text{Ni}_{10}$ . However, this increase is not very dramatic. Further, the  $\Delta T_x$  is relatively constant for levels from 0.20% up to 1.2% oxygen. Although there is a little scatter in the data, most of the

variation can be attributed to measurement error in  $T_g$  and  $T_x$ . The heat of crystallization of the first peak remains constant up to 0.42% oxygen, indicating constant relative glass stability up to these oxygen content levels. Above 0.42% oxygen,  $\Delta H_{first}$  begins to decrease. Of the three alloys reported in this research, the  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  alloy has been studied the least. Work by [25] has shown that the alloy undergoes solute clustering, with anti-segregation of copper and titanium. Further study of the crystallization has revealed decomposition into copper-enriched and titanium-enriched regions, with the nucleation and growth of fcc nanocrystals (with a lattice parameter of  $a = 3.8 \text{ \AA}$ ) containing about 80% titanium and 20% zirconium. Based on the present data, the stability of the undercooled liquid region appears to remain constant. Figure 7 shows a comparison of  $\Delta T_x$  versus oxygen content for various alloys studied in this work and in prior published works. Clearly, the traditional view that oxygen is an impurity and always decreases the glass-forming ability of an alloy is discounted. Indeed, in many Zr-based systems, oxygen does dramatically reduce the undercooled liquid region, but in  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$ , oxygen appears to play a neutral role in the glass-forming behavior and in  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  and  $\text{Zr}_{66.7}\text{Cu}_{33.3}$  it actually improves the glass-forming behavior by increasing  $\Delta T_x$  (up to approx 1.0 at% oxygen).

Oxygen has traditionally been considered a detrimental impurity in metallic glasses. Recent research [7] suggests that oxygen could be regarded as an alloying element in small amounts, although usually with detrimental results. Eckert [21] claimed that the Zr-Al-Cu-Ni alloy could be viewed as a 5-component system in which the dilute component oxygen plays a controlling role in crystallization, leading to phases and microstructures that cannot be achieved in the metallic glass without oxygen. Hence, oxygen may be useful for obtaining new nanostructured multicomponent alloys with interesting properties. The present results further validate the idea that oxygen may be viewed as an alloying element, even if a sensitive one. In addition to the previously established effect on crystallization and microstructure, this work shows that oxygen improves  $\Delta T_x$  of  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  by 10 K (or about 33%).

## 5. Conclusions

The effect of oxygen levels on the stability of  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  bulk metallic glass alloys was studied. For  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ , oxygen is detrimental and decreases  $\Delta T_x$  from over 100 K down to 55 K. Even though this alloy exhibits a large decrease in  $\Delta T_x$ , analysis of the activation energy of crystallization indicates that oxygen could be partially stabilizing the undercooled liquid by promoting the formation of quasicrystalline phases in the melt. This, in turn, inhibits the formation of further crystalline phases. In  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , oxygen had little effect on  $\Delta T_x$ , which remained relatively constant at 45 K for oxygen contents up to 1.2 at%. In  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , oxygen levels up to 0.80 at% were shown to be beneficial by increasing  $\Delta T_x$  from 31 K to 38 K. This is the first evidence that oxygen can be a beneficial alloying element in bulk metallic glasses by stabilizing the supercooled liquid region and improving glass-forming ability.

## Acknowledgements

The authors are grateful to B. Smith for sample preparation and O. Senkov and J. Warner for assistance with thermal data analysis. This research was supported under AFOSR Task 01ML05–COR (Dr. C. Hartley, Program Manager).

## References

- [1] Inoue A. Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Mater* 2000;48:279-306.
- [2] Lin XH, Johnson WL, Rhim WK. Effect of oxygen impurity on crystallization of an undercooled bulk glass forming Zr-Ti-Cu-Ni-Al alloy. *Mater Trans JIM* 1997;38:473-7.
- [3] Inoue A, Shinohara Y, Yokoyama Y, Masumoto T. Solidification Analyses of Bulky  $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$  Glass Produced by Casting into Wedge-Shape Copper Mold. *Mater Trans JIM* 1995;36:1276-81.
- [4] Kübler A, Eckert J, Gebert A, Schultz L. Influence of oxygen on the viscosity of Zr–Al–Cu–Ni metallic glasses in the undercooled liquid region. *J Appl Phys* 1998;83:3438.
- [5] Miracle DB. A structural model for metallic glasses. *Nature Mater* 2004;3:697-704.

- [6] Kato H, Kawamura A, Inoue A. High tensile strength bulk glassy alloy Zr<sub>65</sub> Al<sub>10</sub> Ni<sub>10</sub> Cu<sub>15</sub> prepared by extrusion of atomized glassy powder. *Mater Trans JIM* 2000;37:70-7.
- [7] Murty BS, Ping DH, Hono K, Inoue A. Influence of oxygen on the crystallization behavior of Zr<sub>65</sub> Cu<sub>27.5</sub> Al<sub>7.5</sub> and Zr<sub>66.7</sub> Cu<sub>33.3</sub> metallic glasses. *Acta Mater* 2000;48:3985-3996.
- [8] de Oliveira MF, Botta FWJ, Kaufman MJ, Kiminami CS. Phases formed during crystallization of Zr<sub>55</sub> Al<sub>10</sub> Ni<sub>5</sub> Cu<sub>30</sub> metallic glass containing oxygen. *J Non-Cryst Sol* 2002;304:51-55.
- [9] Gebert A, Eckert J, Bauer H-D, Schultz L. Characteristics of slowly cooled Zr-Al-Cu-Ni bulk samples with different oxygen content. *Mat Sci Forum* 1998;269-72:797-802.
- [10] Gebert A, Eckert J, Schultz L. Effect of oxygen on phase formation and thermal stability of slowly cooled Zr<sub>65</sub> Al<sub>7.5</sub> Cu<sub>17.5</sub> Ni<sub>10</sub> metallic glass. *Acta Mater* 1998;46:5475-82.
- [11] Sordellet DJ, Besser MF. Oxygen effects on glass formation of plasma arc sprayed Cu<sub>47</sub> Ti<sub>33</sub> Zr<sub>11</sub> Ni<sub>8</sub> Si<sub>1</sub> surface coatings. *Mat Sci Eng A* 2004;375-7:625-9.
- [12] Xing LQ. Private communication 2004.
- [13] Sun L, Wu Q, Xu Y, Wang W. Study on solidification behaviour of Pd<sub>40</sub> Ni<sub>40</sub> P<sub>20</sub> alloy by fluxing method. *Physica B* 1997;240:205-10.
- [14] Shen TD, Schwarz RB. Bulk ferromagnetic glasses in the Fe-Ni-P-B System. *Acta Mater* 2001;49:837-47.
- [15] Bossuyt S, Madge SV, Chen GZ, Castellero A, Deledda S, Eckert J, Fray DJ, Greer AL. Electrochemical removal of oxygen for processing glass-forming alloys. *Mat Sci Eng A* 2004;375-7:240-3.
- [16] Zhang Y, Pan MX, Zhao DQ, Wang RJ, Wang WH. Formation of Zr-based bulk metallic glasses from low purity of materials by yttrium addition. *Mater Trans JIM* 2000;41:1410-4.
- [17] Choi-Yim H, Busch R, Johnson WL. The effect of silicon on the glass forming ability of the Cu<sub>47</sub> Ti<sub>34</sub> Zr<sub>11</sub> Ni<sub>8</sub> bulk metallic glass forming alloy during processing of composites. *J Appl Phys* 1998;83:7993-7.
- [18] Kundig AA, Lepori D, Perry AJ, Rossmann S, Blatter A, Dommann A, Uggowitzer PJ. Influence of Low Oxygen Contents and Alloy Refinement on the Glass Forming Ability of Zr<sub>52.5</sub> Cu<sub>17.9</sub> Ni<sub>14.6</sub> Al<sub>10</sub> Ti<sub>5</sub>. *Mater Trans JIM* 2002;43:3206-10.
- [19] Liu CT, Chisholm MF, Miller MK. Oxygen impurity and microalloying effect in a Zr-based bulk metallic glass alloy. *Intermetallics* 2002;10:1105-12.
- [20] Lu ZP, Tan H, Li Y, Ng SC. The correlation between reduced glass transition temperature and glass forming ability of bulk metallic glasses. *Scripta Mater* 2000;42:667-73.
- [21] Eckert J, Mattern N, Zinkevitch M, Seidel M. Crystallization behavior and phase formation in Zr-Al-Cu-Ni metallic glass containing oxygen. *Mater Trans JIM* 1998;39:623-32.
- [22] Altounian Z, Batalla E, Strom-Olsen JO, Walter JL. The influence of oxygen and other impurities on the crystallization of NiZr<sub>2</sub> and related metallic glasses. *J Appl Phys* 1987;61:149-55.
- [23] Miracle DB, Senkov ON, Sanders WS, Kendig KL. Structure-forming principles for amorphous metals. *Mat Sci Eng A* 2004;375-377:150-6.

- [24] Kasai M, Matsubara E, Saida J, Nakayama M, Uematsu K, Zhang T, Inoue A. Crystallisation behaviour of Cu<sub>60</sub> Zr<sub>30</sub> Ti<sub>10</sub> bulk glassy alloy. *Mat Sci Eng A* 2004;375-7:744-8.
- [25] Glade SC, Löffler JF, Bossuyt S, Johnson WL, Miller MK. Crystallization of amorphous Cu<sub>47</sub> Ti<sub>34</sub> Zr<sub>11</sub> Ni<sub>8</sub>. *J Appl Phys* 2001;89:1573-9.

## Figure Captions

**Figure 1.** DSC scans for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive heat flows.

**Figure 2.** Selected DSC scans for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive heat flows.

**Figure 3.** DSC scans for  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive heat flows.

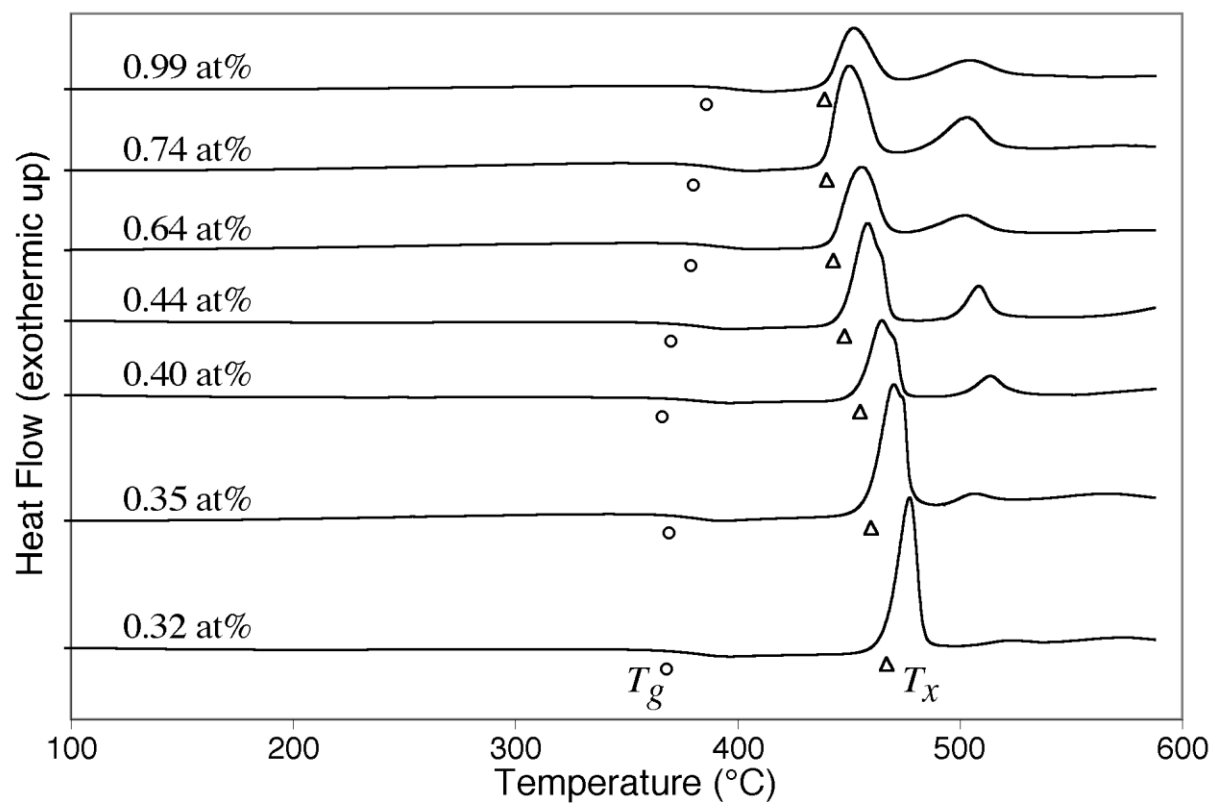
**Figure 4.**  $T_g$  (circles),  $T_x$  (diamonds),  $\Delta T_x$  (triangles) and the heats of crystallization for the first peak  $\Delta H_{first}$  (crosses) and for all peaks  $\Delta H_{all}$  (diagonal crosses) for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$ . All data obtained from samples cast 500  $\mu\text{m}$  thick except data for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  at 1.55 at% oxygen, which was cast 250  $\mu\text{m}$  thick.

**Figure 5.** Activation energy for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  alloys.

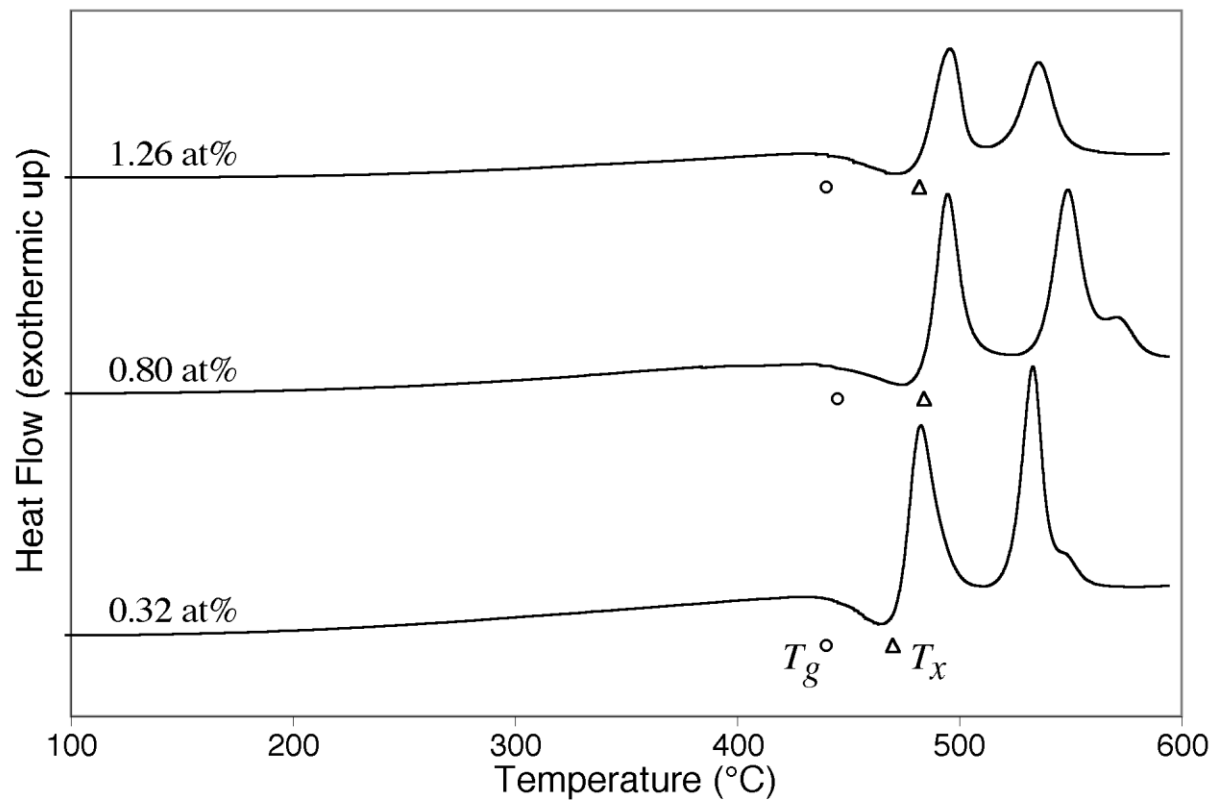
**Figure 6.** DSC scans for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  with 1.26 at% oxygen taken from different areas of the cast strip. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive heat flows.

**Figure 7.** Comparison of  $\Delta T_x$  of alloys studied in this research and by other authors [7, 10]. Only alloys  $\text{Zr}_{66.7}\text{Cu}_{33.3}$  [7] and  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  (from 0.3 to 0.8 at%) show an increase in  $\Delta T_x$  with increasing amounts of oxygen.

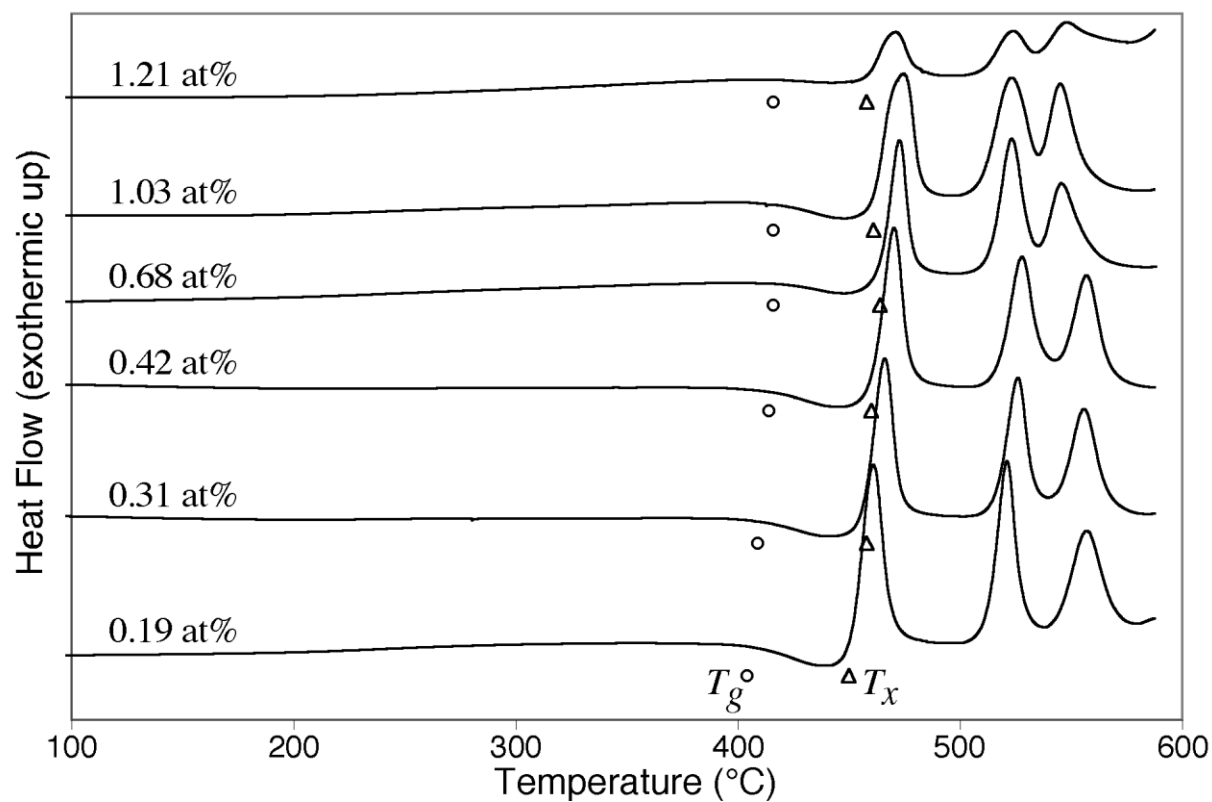
## Figures



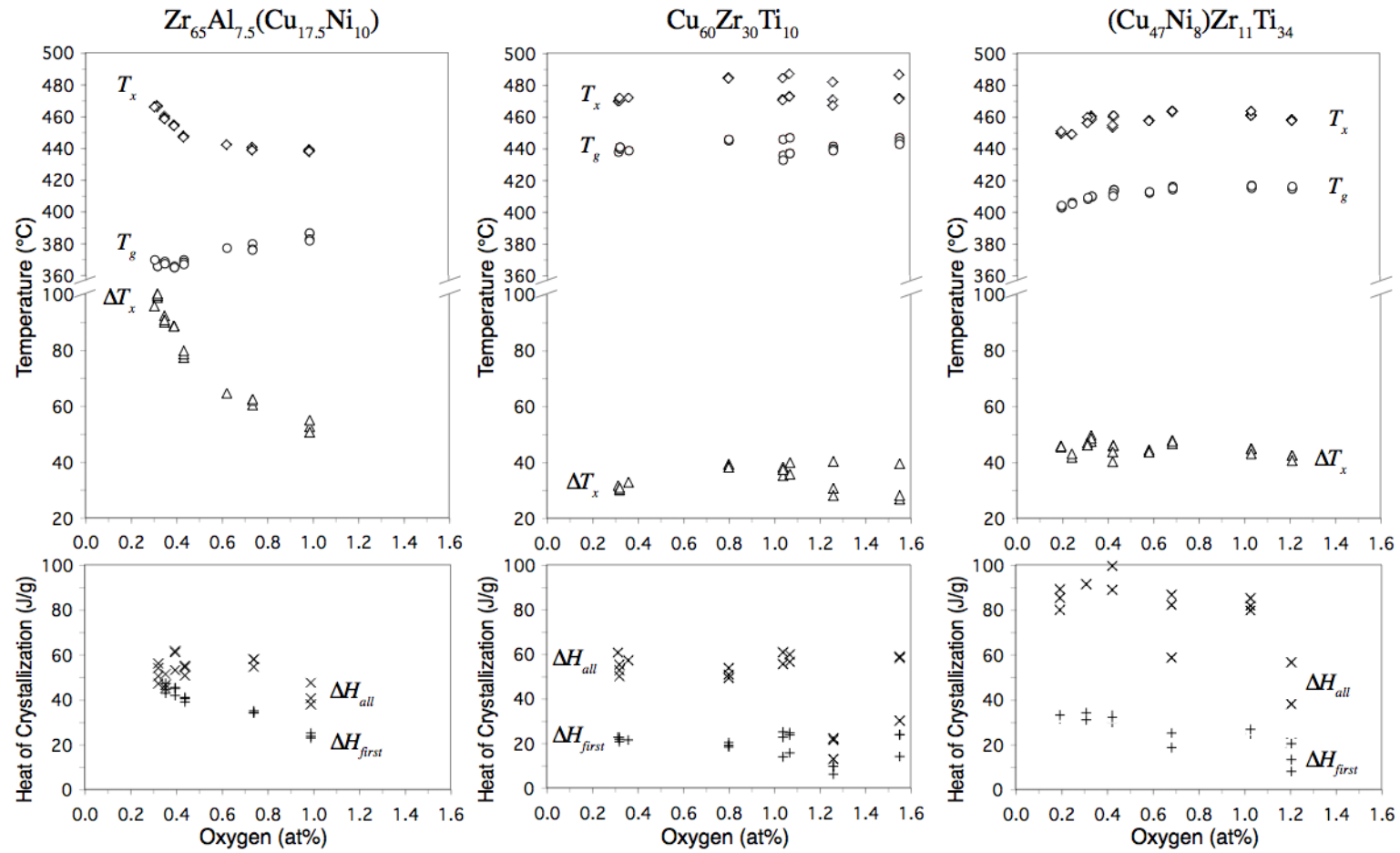
**Figure 1.** DSC scans for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive (upward) heat flows.



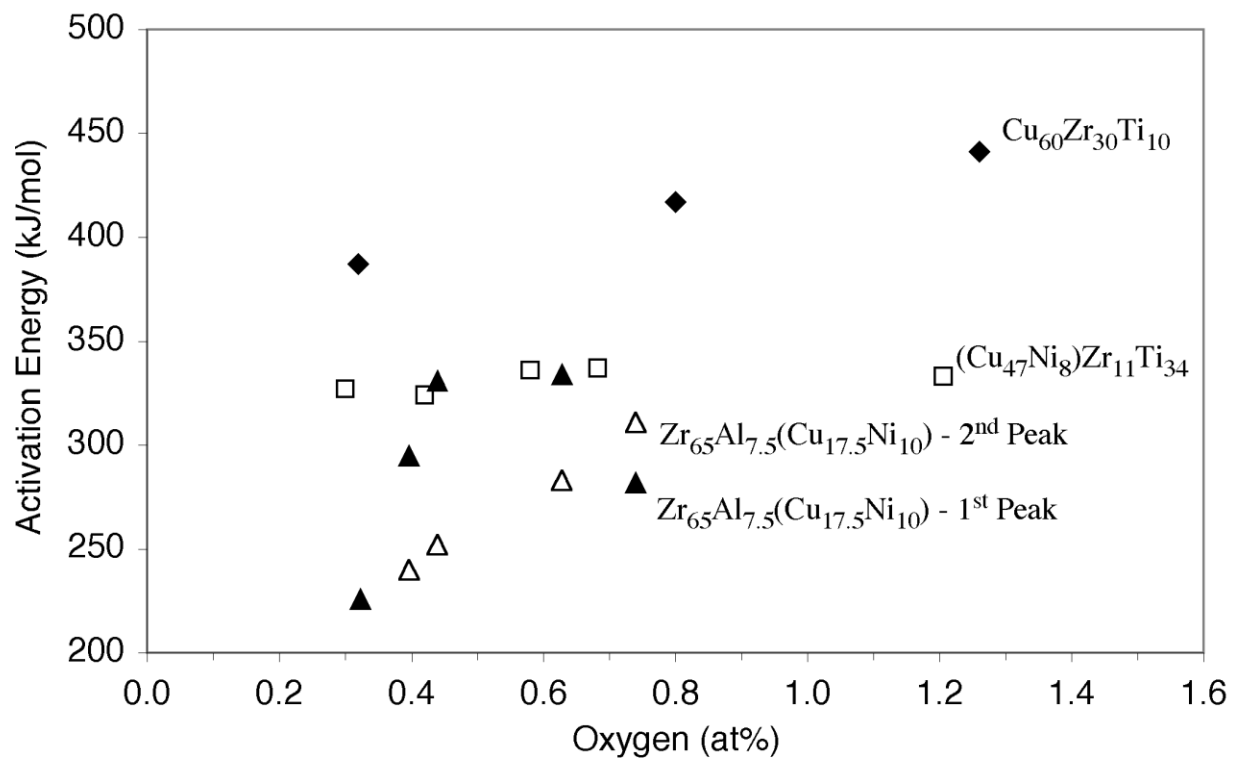
**Figure 2.** Selected DSC scans for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive (upward) heat flows.



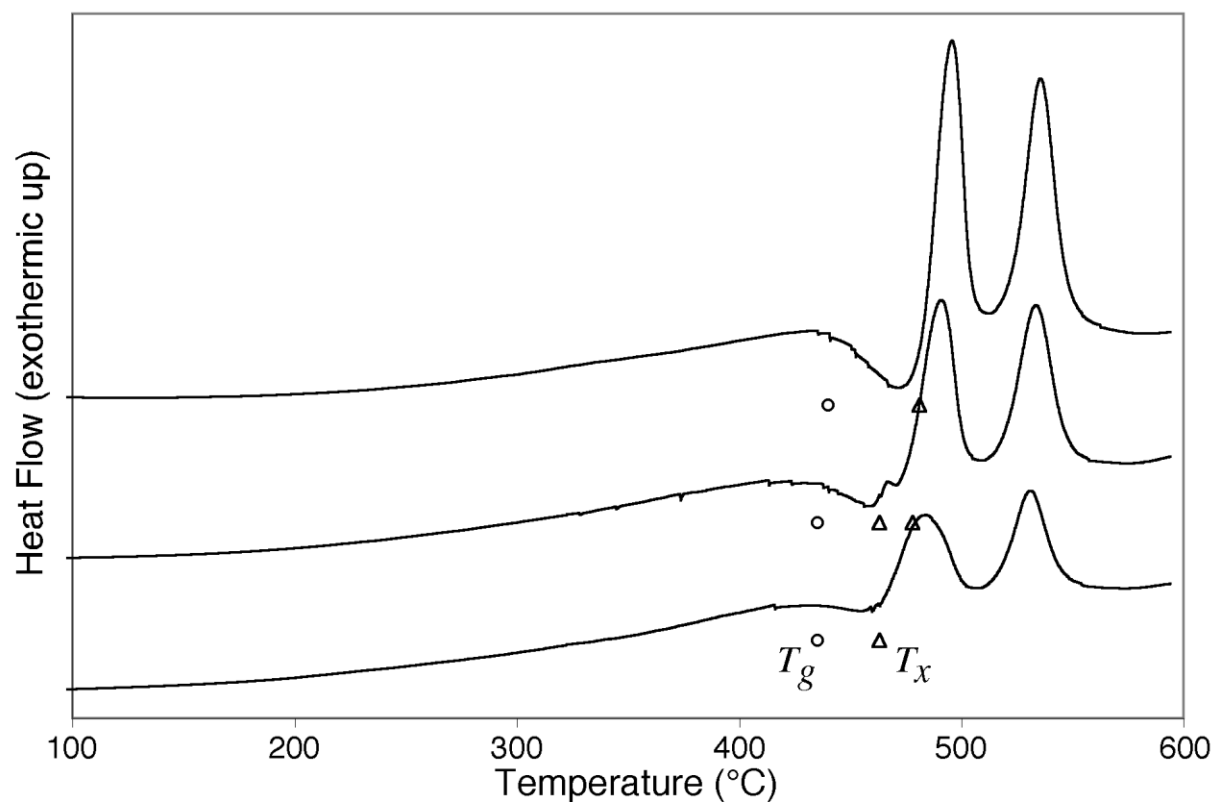
**Figure 3.** DSC scans for  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  heated at  $20 \text{ K s}^{-1}$  with different oxygen content. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive (upward) heat flows.



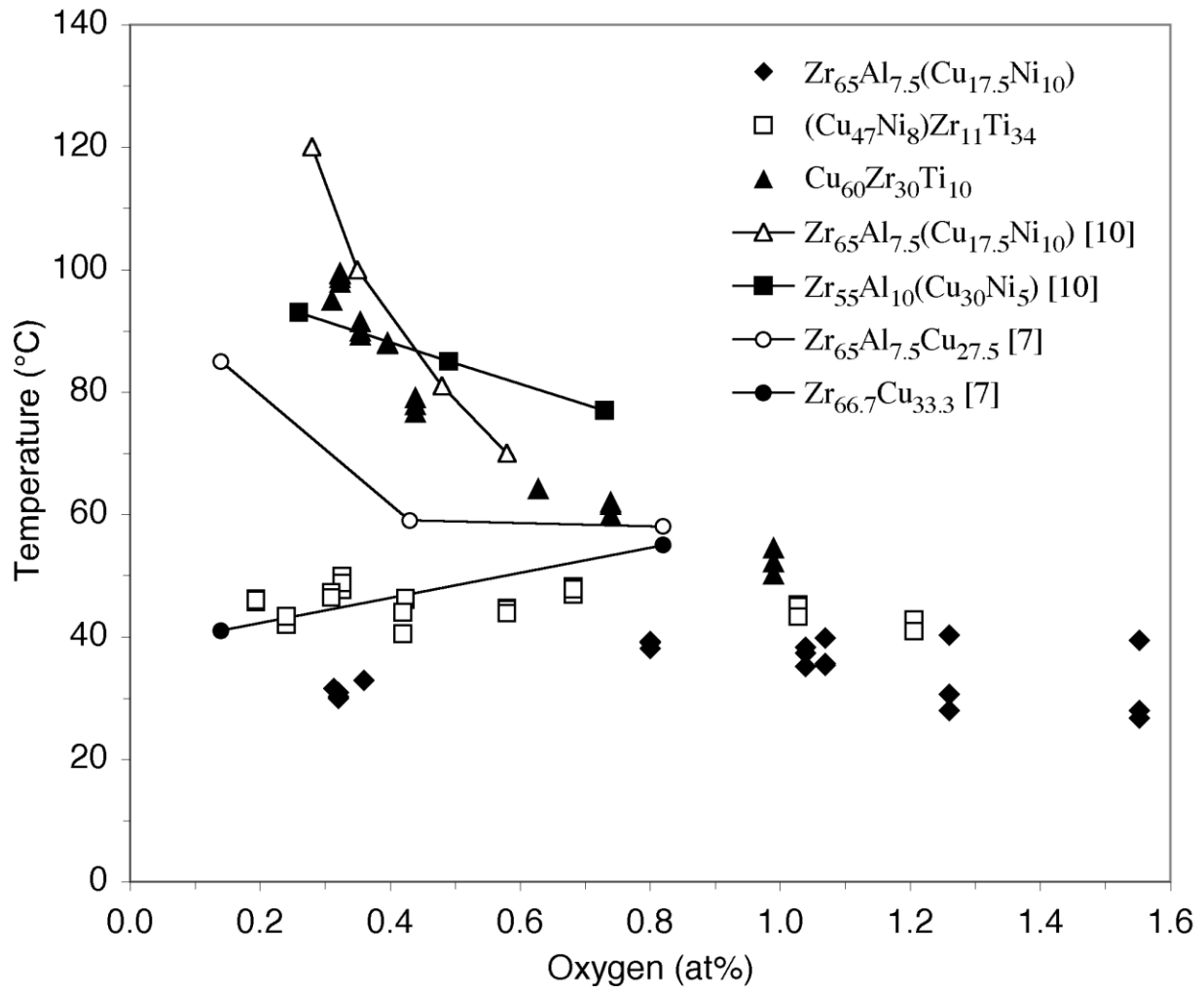
**Figure 4.**  $T_g$  (circles),  $T_x$  (diamonds),  $\Delta T_x$  (triangles) and the heats of crystallization for the first peak  $\Delta H_{\text{first}}$  (crosses) and for all peaks  $\Delta H_{\text{all}}$  (diagonal crosses) for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$ . All data are obtained from cast samples 500  $\mu\text{m}$  thick except data for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  at 1.55 at% oxygen, which was 250  $\mu\text{m}$  thick.



**Figure 5.** Activation energy for  $\text{Zr}_{65}\text{Al}_{7.5}(\text{Cu}_{17.5}\text{Ni}_{10})$ ,  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ , and  $(\text{Cu}_{47}\text{Ni}_8)\text{Zr}_{11}\text{Ti}_{34}$  alloys.



**Figure 6.** DSC scans for  $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$  with 1.26 at% oxygen taken from different areas of the same cast strip. Circles indicate  $T_g$  and triangles indicate  $T_x$ . Exothermic reactions are indicated by positive (upward) heat flows.



**Figure 7.** Comparison of  $\Delta T_x$  of alloys studied in this research and by other authors [7, 10].

Only alloys  $Zr_{66.7}Cu_{33.3}$  [7] and  $Cu_{60}Zr_{30}Ti_{10}$  (from 0.3 to 0.8 at%) show an increase in  $\Delta T_x$  with increasing amounts of oxygen.